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Heat-Resistant Hydrophobic–Oleophobic Coatings

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ABSTRACT: Thermally and chemically durable hydrophobic oleophobic coatings, containing different ceramic particles such as SiO_2, SiC, Al_2O_3, which can be alternative instead of Teflon, have been developed and applied on the aluminum substrates by spin-coating method. Polyimides, which are high-thermal resistant heteroaromatic polymers, were synthesized, and fluor oligomers were added to these polymers to obtain hydrophobic–oleophobic properties. After coating, Al surface was subjected to Taber-abrasion, adhesion, corrosion, and thermal tests. The effects of the particle size of ceramic powders, organic matrix, and heat on the coating material were investigated. Coating material was characterized by FTIR spectrophotometer. Surface properties and thermal resistance of the coating materials were investigated by SEM and TGA analyses. After thermal curing, contact angles of these coatings with H_2O and *n*-hexadecane were measured. It was observed that coatings like ceramic particles are more resistant against scratch and abrasion than the other coatings. Also, they are harder than coatings, which do not include ceramic particles. It was seen that coatings, containing Fluorolink D10H, have high-contact angles with water and *n*-hexadecane.

Key words: hydrophobic-oleophobic coating; heat-resistance; spin-coating; ceramic powder

INTRODUCTION

Nowadays, instead of making coatings that have only one property, it is preferred to make coatings that have more than one property. It can be gained to that coating property like heat and good mechanical resistance, water-repellency (hydrophobic), and oil-repellency (oleophobic).

At present, the field of heat-resistant heteroaromatic polymers has been dominated by polyimides. After several decades of research and development, the polyimides stand almost alone as useful heat-resistant materials. The polyimides are used as films, adhesives, fibers, wire-coating enamels, and resin matrices for composites.[1,2] Polyimides are thermally and chemically stable polymers. Especially, aromatic polyimides have been extensively investigated for their excellent thermal stability and high-mechanical properties, as well as good chemical resistance and electrical properties.[3–6] Most practical routes to obtain polyimides up to early 1970s involved condensation reactions.[7] Synthesis comprises low-temperature polycondensation of a diamine with an aromatic dianhydride in a solvent to yield a soluble intermediate, polyamic acid.[8–12] Films, fibers, or impregnated fibrous reinforcements are produced from this intermediate, which is then converted to cyclized polyimide, either by the reaction of heat (200–300°C)[13–15] or with chemicals,[16–20] for example, carboxylic acid anhydrides in the presence of tertiary amine catalysts as dehydrating agents.

Fluorine-containing polymers have made important contributions as coating materials owing to their low-surface energy and their outstanding properties, such as chemical inertness and thermal stability, in a variety of environments.[20] Fluorine-containing coatings have interesting surface characteristics. Fluorinated monomers can selectively migrate to the interface and can form highly ordered layers on the coating surface, giving rise to surfaces having properties as completely fluorinated polymers,[21] so surface energy decreases. As a result of this, coatings, which are water repellent and oil repellent, can be obtained.

Besides heat resistance and water and oil repellency, for a variety of purposes, filler is compulsory to achieve appropriate properties like strength or wear resistance.[22] If effective bonding between the filler and matrix components occurs, the mechanical properties of polymer composites containing inorganic filler improve.[23]

In this work, thermally and chemically durable hydrophobic–oleophobic coatings, containing different ceramic particles such as SiO_2, SiC, Al_2O_3, which can be alternative of Teflon, have been developed and applied on the aluminum substrates by spin-coating method. After coating the Al plates, abrasion, scratch, adhesion, and corrosion resistance tests were performed. The effects of ceramic powder type and coreactant type (PDA and BTA) on the quality of coating material were also investigated.

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EXPERIMENTAL

Chemicals and apparatus

Pyromellitic dianhydride (PDA) (Fluka), Benzophenone-3,3′-4,4′-tetracarboxylic dianhydride (BTA) (Fluka), and 4,4′-bis(3-aminophenoxy) diphenyl sulfone (BAPPS) (Avacado) were used as starting compounds without further purification. 1-Methyl-2-pyrrolidone (Merck) was used as solvent for BAPPS. Fluorolink D10H (Solvay Solexis) was used to obtain hydrophobic and oleophobic surfaces against water and *n*-hexadecane (Merck). HCl (Merck) and NaOH (AK Chemical) solutions were used in chemical corrosion tests. To protect the metal surfaces, ceramic powders providing mechanical (Taber-abrasion) and chemical resistance to heat were used in these forms: Martoxid Al_2O_3 (Martinswerk-CS 400 MR 200 Ø: ~1.8 μm), SiC (H.C. Starck, Ø: 1.8 μm), SiO_2 (Silbond EST (modified with epoxy silane) 300 Quarzwerke, Ø: 6 μm), and SiO_2 (Silbond EST (modified with epoxy silane) 600 Quarzwerke, Ø: 4 μm). Al-plate was cleaned with 3% solution of P3 Almeco 18 using ultrasonic bath at 70°C for 5 min, and then dried prior to coating.

The coating solutions were characterized using FTIR (Brucker IFS 25) spectrophotometer and element analyzer. Surface properties of coated Al-plate were monitored by using scanning electron microscopy (SEM, JEOL JXA-840A). Thermal resistance of the coating materials were analyzed by thermal analysis systems (DTA/TGA, BAHR-Thermoanalysis GmbH, STA 501). The abrasion resistance was measured using Taber Abraser 5131 (Taber Industries; CS 10F rolls, 5.4 N). The scratch resistance was determined using Multi Cross Cutter (Erichsen, type 295), which was pulled over the coating with 500 g weights. Adhesion of the coating was determined by lattice cut/tape test (Erichsen, ASTM D 3359). The chemical corrosion test was performed by Erichsen Corrosion Testing Instrument SOLVENTCHECKER 434 using HCl (pH: 2) and NaOH (pH: 12) solutions at 60°C for 1 h.

Procedure

Al-plate surfaces were separately coated with coating solutions either containing ceramic powders or not. For this purpose, (I) the amount of Fluorolink D10H required to achieve the best hydrophobic–oleophobic property was examined, (II) coating solutions were prepared by adding ceramic powders, to investigate effects of ceramic powders on the resistance properties of surfaces, and (III) the experiments described earlier were repeated by substituting PDA used in II with BTA to provide mechanical (Taber-abrasion) resistance to heat-treated Al-plate surfaces.

Preparation of hydrophobic and oleophobic surfaces without using ceramic powders

After dissolving 4,4′-bis(3-aminophenoxy) diphenyl sulfone (BAPPS) in 1-methyl-2-pyrrolidone (NMP), the required amount of Fluorolink D10H (w/w, %, relative to solid) was added, and the mixture was stirred for 30 min. Then, the required amount of PDA (mol) was added, and the final mixture was stirred overnight at room temperature. Al-plates (10 × 10 cm^2) were coated with this solution using spin-coating technique (500 cycles/min) for 10 s. They were thermally treated at 200°C for 90 min to harden the coating. Contact angles of water and *n*-hexadecane on the heat-treated Al-plates were measured before and after abrasion test (200 cycles). Hydrophobic contact angle, oleophobic contact angle, after Taber test hydrophobic contact angle and oleophobic contact angle referred to hereafter as HCA, OCA, THCA, and TOCA, respectively.

Preparation of hydrophobic and oleophobic surfaces using ceramic powders

The amounts of BAPPS and NMP were kept constant for further experiments, in which 11.5% (w/w, relative to solid) of Fluorolink D10H and 0.076 mol of

TABLE I
Effect of the Amount of Fluorolink D10H on Contact Angle of Water and *n*-Hexadecane, Film Thickness and Weight Loss of Coated Al-Surfaces Before and After Taber-Abrasion Test

Mixture	Fluorolink D10H (%, w/w)	PDA (mol)	HCA[a]	THCA[b]	OCA[a]	TOCA[b]	Film thickness (μm)	Weight loss at 200°C (mg)
1	4.55	0.0728	99	75	55	30	3.2	2.2
2	8.67	0.0736	101	86	60	40	3.3	1.9
3	12.43	0.0744	102	87	60	40	4	2.0
4	15.86	0.0752	102	85	59	44	3.8	2.4
5	19.01	0.076	102	86	60	44	3.9	2.5
6	21.91	0.0768	102	86	55	44	3.7	3.1
7	24.6	0.0776	102	88	55	44	4	3.6

Surface preparation conditions: 31.14 g BAPPS, 200 g NMP, at 200°C.
[a] As obtained after heat treatment.
[b] After 200 cycles Taber test.

TABLE II
Effect of Ceramic Powder Addition on the Contact Angles, Film Thickness, and Weight Loss of Coated Al-Surfaces Before and After Taber-Abrasion (1000 cycles) Tests

Mixture	Ceramic powder	HCA		THCA		OCA		TOCA		Film thickness (m)		Weight loss at 200°C (mg)	
		a	b	a	b	a	b	a	b	a	b	a	b
1	SiC	106°	105°	85°	87°	60°	62°	57°	57°	7.7	21	1	1.4
2	Silbond 300 EST	106°	102°	80°	75°	65°	61°	48°	50°	10.5	19.1	13.7	11.6
3	Silbond 600 EST	108°	110°	80°	78°	60°	65°	50°	53°	7.4	21.2	8.3	31.6
4	Martoxid Al_2O_3	103°	102°	81°	79°	59°	61°	53°	55°	6	17	1.4	0.5

Surface preparation conditions: 31.14 g BAPPS, 200 g NMP, 11.5% (w/w) Fluorolink D10H, 0.076 mol of PDA or BTA, 40% (w/w) ceramic powders, heat treatment at 200°C.
a: Measurements were realized with PDA[4]
b: measurements were realized with BTA.

PDA were used. 40% of ceramic powders, such as SiC, Silbond 300 EST, Silbond 600 EST, and Martoxid Al_2O_3, were separately added (w/w, relative to total solid) into the final mixture, and then dispersed for 2 h with roller balls operated at 3000 rpm. Finally, Al-plates were coated with these ceramic powder-containing solutions. Contact angles of water and *n*-hexadecane on the coated Al-plates treated at 200, 250, and 300°C for 90 min were measured before and after abrasion tests (1000 cycles). The experiments were repeated by substituting BTA with PDA.

RESULTS AND DISCUSSION

The amount of Fluorulink D10H required to achieve the best hydrophobic and oleophobic surfaces and some of their properties are shown in Table I. The effect of ceramic powder addition into on contact angle, film thickness, and weight loss of coated Al-plate surfaces heated at 200, 250, and 300°C are shown in Tables II and III, respectively.

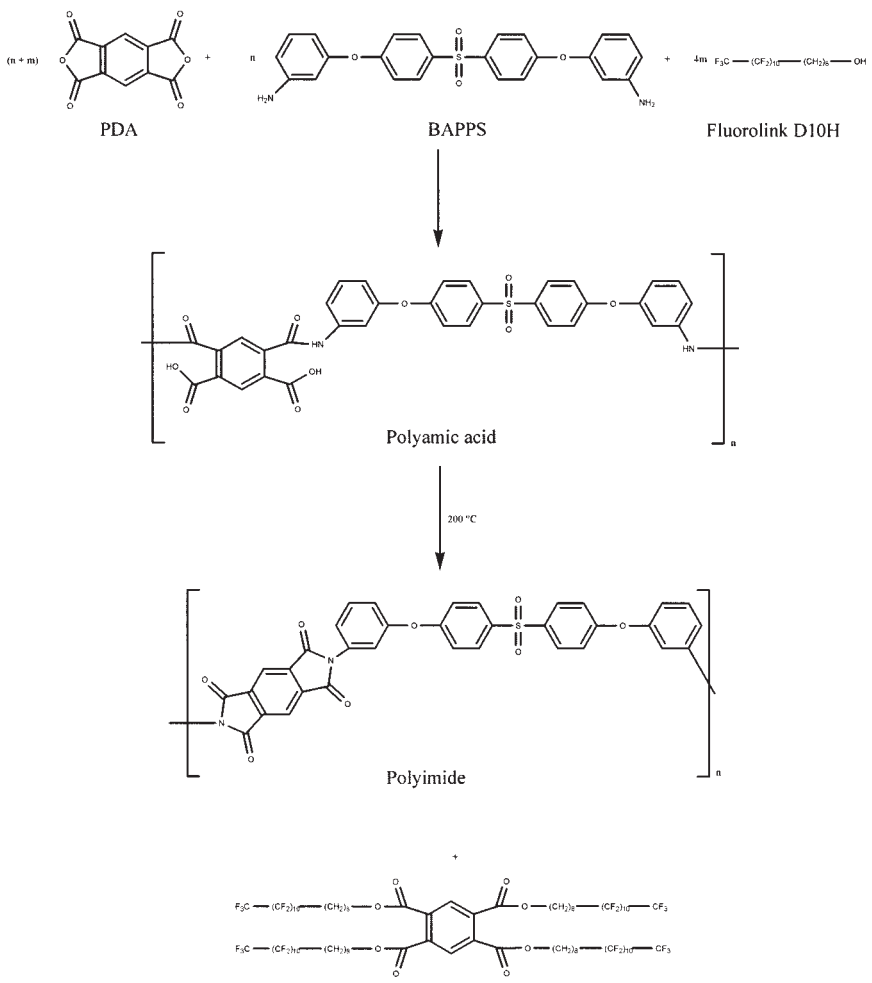
It is seen that the change of the values of THCA, OCA, and TOCA is actually related to the amount of Fluorolink D10H (Table I). According to Table I, it was seen that contact angles were almost fixed when the ratio of Fluorolink D10H was used between 12.43 and 24.6% (w/w %). The cracking and high weight loss occurred on the coated surface when Fluorolink D10H was at 15.86 and 24.6% (w/w %). The lower the amount of Fluorolink D10H, the lowest the contact angle was, and it was seen that they were fixed after Taber-abrasion tests. However, the coated surfaces acquired a good hydrophobic and oleophobic property before and after Taber-abrasion tests when the amount of Fluorolink D10H were at 8.67 and 12.43% (w/w %).

It is well-known that inorganic network is harder than organic network, and hardness can be raised by addition of ceramic powders into the organic matrix. As seen from the Table I, the weight loss of coated surfaces prepared in the absence of ceramic powders dramatically raised after 200 cycles of Taber abrasion test. According to the results given in Table II, the

TABLE III
Effect of Temperature on Contact Angles, Film Thickness, and Weight Loss of Coated Al-Surfaces Obtained After Treatment 200°C Before and After Taber-Abrasion (1000 cycles) Test

Mixture no	Ceramic powder	HCA, a/b	THCA, a/b	OCA, a/b	TOCA, a/b	Film thickness (μm), a/b	Weight loss (mg), a/b
1[a]	SiC	104°/108°	76°/79°	61°/62°	46°/49°	7.5/7.2	0.9/3.6
2[a]	Silbond 300 EST	103°/114°	80°/76°	62°/66°	50°/49°	10.4/8.7	14.1/12.6
3[a]	Silbond 600 EST	103°/111°	78°/72°	62°/65°	53°/50°	7.6/7.8	7.3/7.4
4[a]	Martoxid Al_2O_3	105°/98°	77°/80°	61°/60°	43°/43°	5.7/5.6	7.9/6.4
5[b]	SiC	107°/98°	82°/82°	62°/60°	54°/54°	20/21	2.2/1.9
6[b]	Silbond 300 EST	106°/104°	90°/86°	63°/62°	55°/50°	19.6/19.4	7.4/6.4
7[b]	Silbond 600 EST	104°/106°	88°/88°	63°/60°	58°/55°	22/22	13.6/13.4
8[b]	Martoxid Al_2O_3	106°/104°	78°/76°	56°/54°	51°/50°	17/16.7	0.2/0.3

(Surface preparation conditions: 31.14 g BAPPS, 200 g NMP, 11.5% (w/w) Fluorolink D10H, 0.076 mol of PDA or BTA, 40% (w/w) ceramic powder, coated surfaces treated at 250 and 300°C)
a: 250 °C; b: 300 °C.
[a] With PDA.
[b] With BTA.



Scheme 1

surface coated in the presence of ceramic powders has very good abrasion resistance after 1000 cycles and weight losses are the lower than the other coated surface. These results also showed that particle size of ceramic powder significantly affects the quality of the coatings. If the ceramic powders with coarser particle sizes (i.e., Silbond EST 300 and Silbond EST 600) were added, the quality of coating was getting worse, the surfaces were rough, the resistance to Taber-abrasion of coated surfaces decreased, the weight losses were

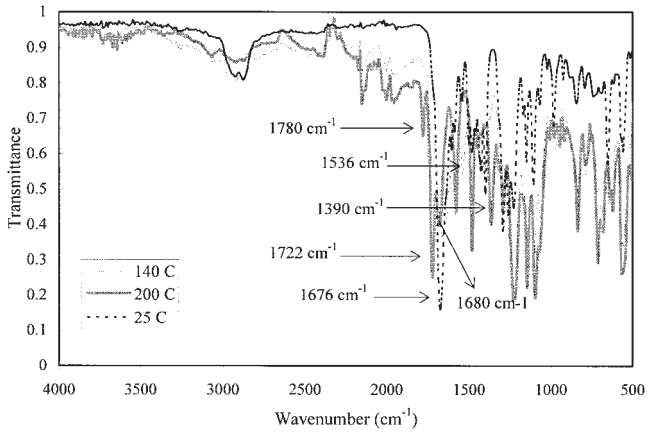


Figure 1 The FTIR spectra of BAPPS/NMP/Fluorolink D10H/BTA mixture at 25, 140, and 200°C.

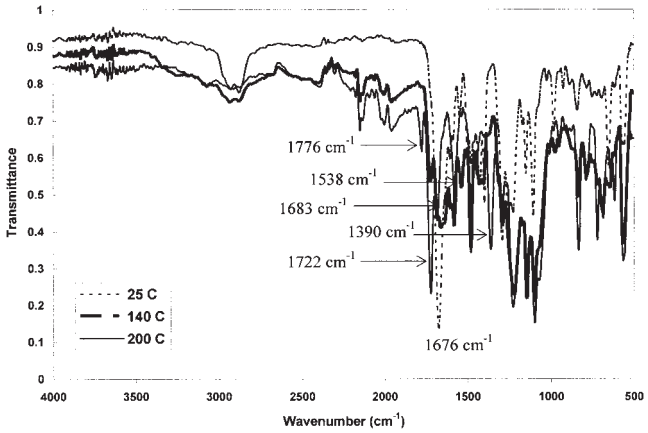


Figure 2 The FTIR spectra of BAPPS/NMP/Fluorolink D10H/PDA mixture at 25, 140, and 200°C.

TABLE IV
TGA Results of the Dried Solids at 200°C for 2 and 18 h, Respectively

	Weight loss (%)		Temperature (°C)	
Sample	2 h	18 h	2 h	18 h
1	12.5	1.0	380	170
2	12.5	1.0	400	170
3	10	0.8	380	150
4	7.5	0.5	250	150

high, and the contact angles of water and *n*-hexadecane were low.

In the coatings prepared with fluor, it is necessary to rise the fluor atoms to the surface to obtain a surface with good hydrophobic and oleophobic.[24] The coatings, which have good hydrophobic and oleophobic property and much resistance to Taber-abrasion test, were obtained from the mixture of Fluorolink D10H/PDA/SiC, Fluorolink D10H/PDA/Al_2O_3, FluorolinkD10H/BTA/SiC and Fluorolink D10H/BTA/Al_2O_3 (Table II, mixtures: 1 and 4).

Reasons for this can be explained by heterogeneous distribution of Fluorolink D10H in the coating and strong adhesion of the coatings on the surface, which is facilitated by the attraction of fluor atoms by the metal.

When the coated surfaces treated at 250 and 300°C for 1 h are considered, the best results were obtained with Fluorolink D10H/PDA/SiC, Fluorolink D10H/PDA/Al_2O_3, FluorolinkD10H/BTA/SiC and Fluorolink D10H/BTA/Al_2O_3 coatings.

Chemical corrosion tests, which are performed against HCl (pH = 2) and NaOH (pH = 12) solutions at 60°C for 1 h, indicated that no change was observed on the surface properties; all the coated surfaces have high resistance.

The scratch and adhesion test performed according to the ASTM D 3359 standard test indicated that the results is 5B for the coating prepared with Fluorolink D10H. After scratching the freshly coated surface, there were no disintegrations and no wears, and no coating material was adhered to the tape after scratching.

Synthesis comprises low-temperature polycondensation of a diamine with an aromatic dianhydride in a solvent to yield a soluble intermediate, polyamic acid. Films, fibers, or impregnated fibrous reinforcements are produced from this intermediate, which is then converted to cyclized polyimide by the reaction of heat (200–300°C). The reaction occurred between PDA, BAPPS, and Fluorolink D10H can be estimated, as shown in Scheme 1.

The FTIR spectra of the coating solutions prepared from BAPPS/NMP/Fluorolink D10H/BTA and BAPPS/NMP/Fluorolink D10H/PDA mixtures recorded at 25, 140, and 200°C are shown in Figures 1 and 2, respectively.

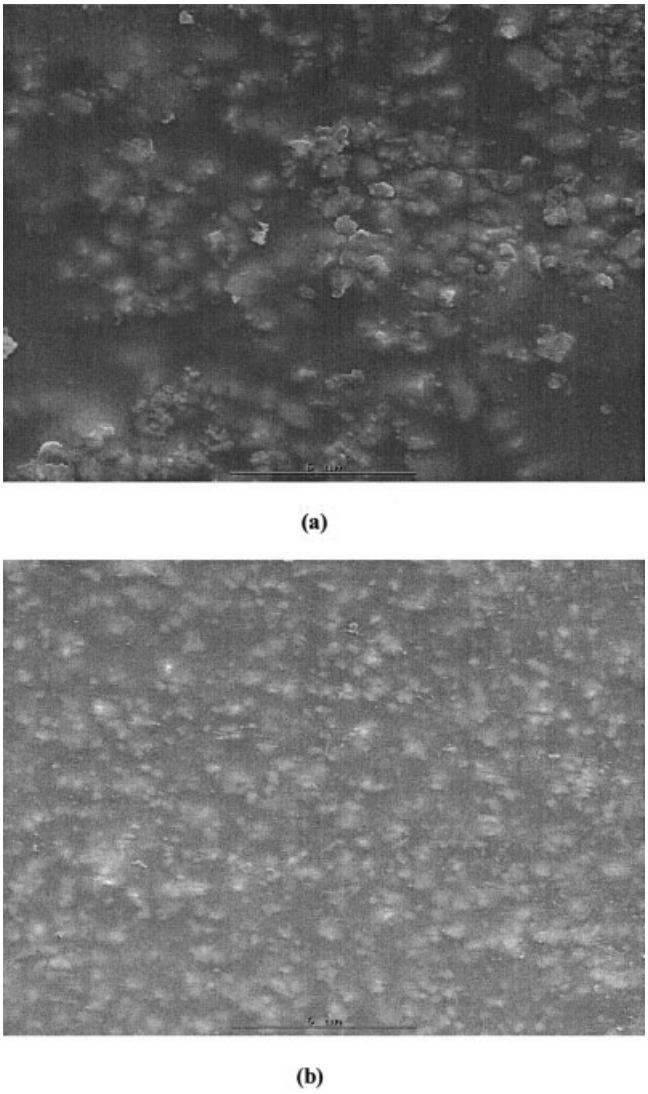


Figure 3 The SEM microphotographs of (a) BAPPS/NMP/Fluorolink D10H/BTA/SiC and (b) BAPPS/NMP/Fluorolink D10H/BTA/Martoxid Al_2O_3 coated Al-plates.

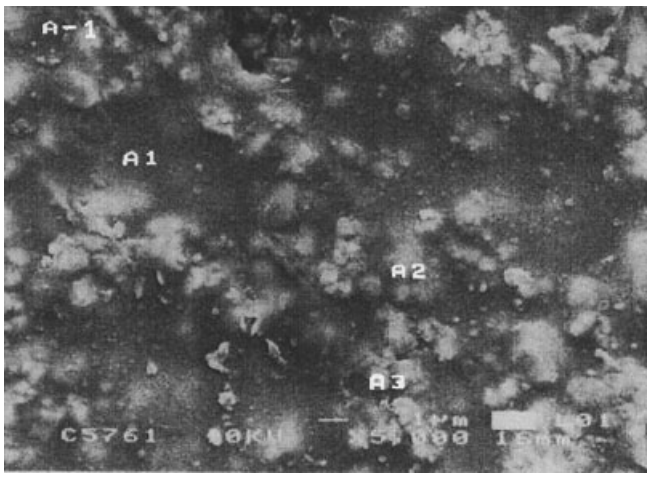


Figure 4 Three selected points for elemental analysis on the BAPPS/NMP/Fluorolink D10H/BTA/SiC coated Al-plate.

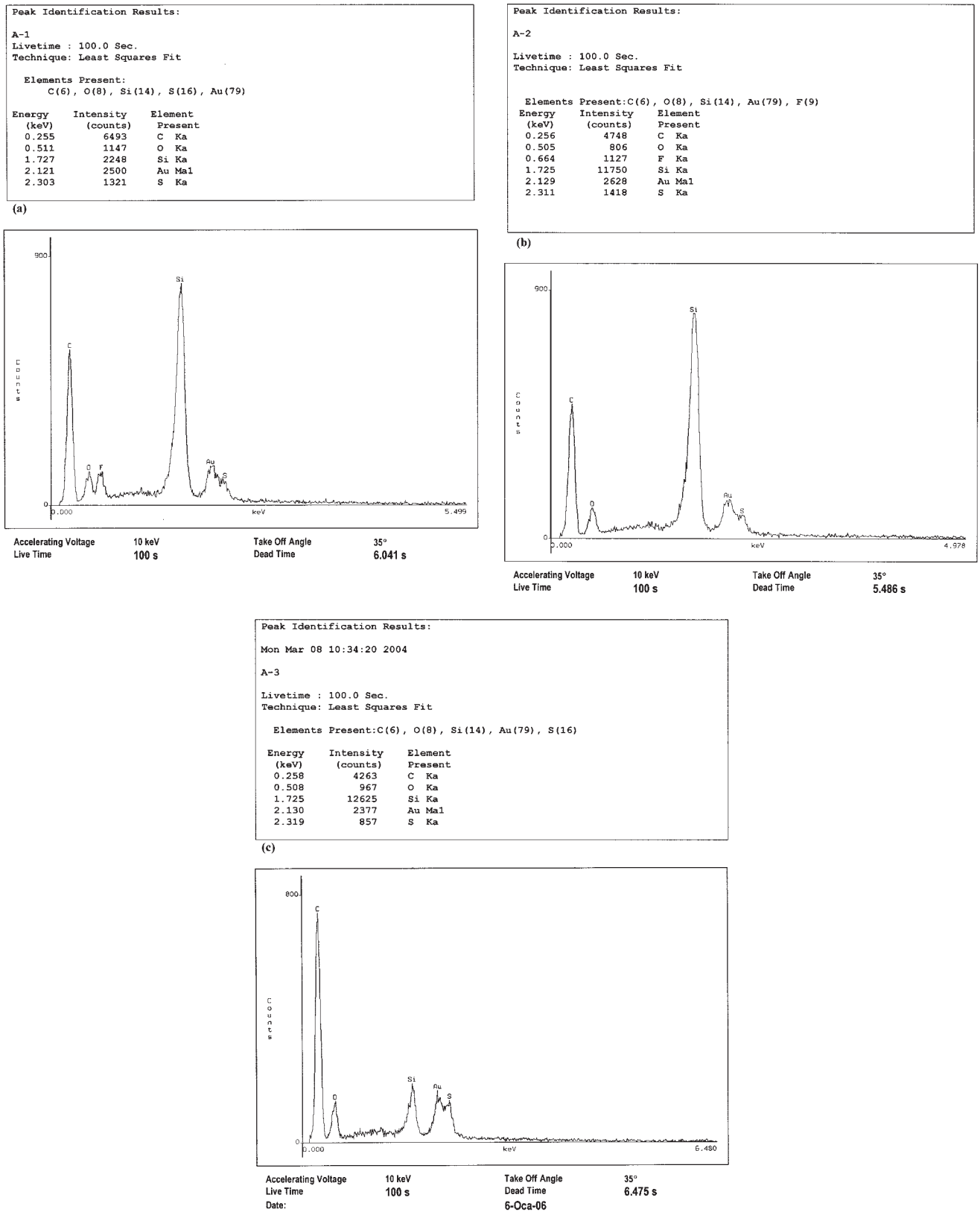


Figure 5 The elemental analysis results in the selected A-1 point (a), A-2 point (b), and A-3 point (c).

The peak due to the stretching vibration of the CO group of amide was observed at 1676 cm^{-1} at 25°C. However, the same stretching vibration of CO group of 1-methyl-2-pyrrolidone is also observed at this region. The intensity of this peak decreases largely at 140 and 200°C, but does not fully disappear. This may be

due to insufficient removal of the solvent or to stretching vibration of CO group of diaryl ketone found in the reaction media can observed at 1676 cm^{-1}. The imide begins to form in both of the mixtures at 140°C (Figs. 1 and 2). The peaks due to the νCO_{sym} at 1722 cm^{-1}, νCO_{asym} at 1780 and 1776 cm^{-1} show the imide formation. The characteristic νCO_{asym} (1850 cm^{-1}) and νCO_{sym} (1780 cm^{-1}) peaks of five-membered anhydrides were not observed in the FTIR spectra. This result shows complete reaction of all anhydrides.

Thermal resistance of the coating materials, which have the best coating properties after all tests, such as BAPPS/NMP/Fluorolink D10H/BTA/SiC (sample 1), BAPPS/NMP/Fluorolink D10H/BTA/Martoxid Al_2O_3 (sample 2), BAPPS/NMP/Fluorolink D10H/PDA/SiC (sample 3), and BAPPS/NMP/Fluorolink D10H/PDA/Martoxid Al_2O_3 (sample 4) were analyzed by thermal analysis system. TGA measurements were performed at two different conditions. First, the coating mixtures were dried at 200°C for 2 h, and afterwards were dried for 18 h. The results are given in Table IV.

TGA measurements showed that these coating mixtures have high-thermal resistance. According to the Table IV, it was seen that the weight losses of samples dried for 2 h were higher than those dried for 18 h. This is due to the samples dried for 2 h, including some amount of solvent. Namely, the solvent does not fully remove. This result is consistent with the results obtained with IR-measurements at 200°C (Figs. 1 and 2). After the sample was dried for 18 h, the weight losses were found to be as 0.5 and 1% at low temperatures. This is caused by the removal of water physically adsorbed on the solid surface.

The SEM microphotographs of BAPPS/NMP/Fluorolink D10H/BTA/SiC and BAPPS/NMP/Fluorolink D10H/BTA/Martoxid Al_2O_3 coated Al-plates are shown in Figure 3(a,b), respectively.

The ceramic particles collected denser in some region on the surface [Fig. 3(a)] and less dense in some region, although the particles dispersed homogeneously in the matrix on the surface present on the surface. According to Taber-abrasion test, it was observed that the surfaces were more homogeneous (Table II and III). Al_2O_3 particles fully dispersed in the matrix on the surface. In addition, it was also seen that Al_2O_3 particles are smaller than SiC particles [Fig. 3(b)].

The results of element analysis carried out locally on the BAPPS/NMP/Fluorolink D10H/BTA/SiC coated Al-plate and in three selected points are given in Figures 4 and 5(a–c).

By chance, if the analysis point met with Al_2O_3, element analysis resulted with higher Al, or if the powders is SiC, it resulted with higher Si levels [Fig. 4(a–d)]. At the points where the ceramic powder are less, carbon levels were found high; however, flour was not determined in general, except for the point A2 [Fig. 4(b)], since amount of the flour compound used was low.

CONCLUSION

In this work, thermal, abrasion, scratch, and chemical resistant coated surfaces have been prepared from synthesized new coating materials containing fluor and ceramic powder on the Al-plates using spin-coating technique. These coated Al-plates can be used as alternative materials, instead of Teflon, because they have good resistant properties described earlier, hydrophobic and oleophobic properties.

When the ceramic powders with coarser particle sizes (i.e., Silbond EST 300 and Silbond EST 600) were added in the organic matrix, the quality of coating was getting worse, the surfaces were rough, the resistance to Taber-abrasion of coated surfaces decreased, the weight losses were high, and the contact angles of water and *n*-hexadecane were low, because these particles were dispersed unhomogeneously. The contact angles of Fluorolink D10H coated surfaces against water and *n*-hexadecane are sufficiently high. SiC and Martoxid Al_2O_3 coated surfaces have better mechanical properties than the other coated surfaces.

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